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Determination of beryllium in a stream sediment by high-performance chelation ion chromatography

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Abstract

High-performance chelation ion chromatography (HPCIC), involving a chelating silica substrate bonded with aminomethylphosphonic acid, has been developed as a novel technique for the quantitative determination of beryllium in complex matrices. An isocratic separation method, using an eluent containing 1 *M* KNO_3, 0.5 *M* HNO_3 and 0.08 *M* ascorbic acid, allowed the Be^{2+} to elute away from the sample matrix peak in under 6 min in a sample containing in excess of 800 mg l^{-1} matrix metals. A detection limit of 35 μg l^{-1} Be(II) was found using a post-column reaction involving Chrome Azurol S (CAS), 1 *M* hexamine and 10 m*M* EDTA buffered at pH 6. The standard addition curve gave excellent linearity (R^2>0.999). The procedure was applied to the determination of trace beryllium in a certified sediment sample. The results obtained compared well with the certified value for beryllium.

Keywords: Beryllium; Aminophosphonate-bonded silica

1. Introduction

It is becoming increasingly recognised that certain trace metals with toxicological properties are having a significant and often detrimental environmental impact.

Beryllium is known to be carcinogenic through its binding to specific regulatory proteins in cells and subsequent accumulation in mammalian cells [1]. The continued use of this toxic element and its compounds by the nuclear, aerospace and metallurgical industries, in addition to its emission during the combustion of fossil fuels, has therefore led to a requirement for analytical methods suitable for the determination of this trace metal in environmental samples.

There are many techniques currently available for the determination of beryllium at low concentrations, of which micellar electrokinetic chromatography coupled to capillary electrophoresis [2] and a beryllium-selective electrode [3] are two which have been developed recently. From the literature, atomic spectrometry appears to be the method of choice because of its simplicity and potential for high sensitivity and accuracy [4–8]. Nevertheless, complex samples can cause matrix interferences which require preconcentration and/or separation steps to be incorporated into the analysis.

In contrast, there are very few methods available for the determination of beryllium by high-performance liquid chromatography (HPLC) [9] and ion

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chromatography (IC) [10–12], the latter a potentially cost effective technique suitable for the study of metals and their speciation. Unfortunately, IC also suffers from the problems associated with complex samples. However, these matrix problems can be overcome by so-called high-performance chelation ion chromatography (HPCIC) which has become a valuable analytical tool for the determination of trace metals in complex matrices. HPCIC involves a different type of sorption mechanism to conventional ion exchange, whereby the metal separation is controlled by the thermodynamics and kinetics of metal complex formation and dissociation on the surface of the stationary phase, normally referred to as ''chelation exchange''.

The relative insensitivity of this exchange mechanism to ionic strength has allowed the determination of metals in various complex samples including selected transition and heavy metals in seawater [13] and the alkaline earths in saturated brines [14]. An advantage of HPCIC is that control of metal selectivity is much wider than that associated with simple cation exchange. This is because the dominant factor associated with the separation of metal ions by chelation is the value of the metal conditional stability constant. As most chelating ligands are conjugate bases of weak acid groups, and have a very strong affinity for hydrogen ions, pH can be used to ''fine tune'' the magnitude of the conditional constant and hence the separation speed and selectivity. The chelation sorption mechanism has also been exploited for the determination of strontium in milk powder [15] and trace bismuth in lead [16] which additionally exemplifies the advantage of this technique for the determination of one metal in a vast excess of another. A recent comprehensive review of HPCIC is given by Jones and Nesterenko [17], which details the historical development of the technique and discusses in depth the reasons for the improvement in separation efficiencies over the last decade.

An earlier paper detailing the determination of beryllium (Be) in environmental matrices using HPCIC is given by Voloschik et al. [18]. The method incorporated a chelating iminodiacetate (IDA) sorbent together with an acidified complexing eluent containing dipicolinic acid with direct conductimetric detection. However, the selectivity of this chromatographic system was not too high and beryllium eluted just after the alkaline earth metals and thus strongly restricts the variety of possible samples for analysis.

Recently, we reported on the chromatographic behaviour of the alkaline earths and selected transition and heavy metals on a novel high-performance chelating aminomethylphosphonic acid-functionalised silica column (APAS) [19]. This substrate exhibited unique selectivity characteristics including an unusual S shaped variation in the plot of capacity factors against pH, demonstrating a change in coordination type with increasing pH. Furthermore, the aminomethylphosphonic acid group showed an increased affinity for certain transition metals, particularly Mn(II) at low pH, which is unusual, as with most chelating groups, including IDA functionality, this metal is very weakly retained. The ability of the aminophosphonate functional groups to serve as an O,O ligand, a type which is favoured by small highly charged metal ions, potentially makes APAS a useful and versatile new phase for the HPCIC of beryllium.

The following paper presents some of the latest studies into the retention behaviour of selected metals on APAS using a high ionic strength eluent with varying pH, and the subsequent development of a method for the determination of beryllium in a certified stream sediment (GBW07311). The procedure was optimised to eliminate large amounts of interferences from metals and other elements present in the sample, and the analytical performance characteristics evaluated.

2. Experimental

2.1. Instrumentation

The isocratic ion chromatographic system consisted of a Dionex GP40 gradient pump (Dionex, Sunnyvale, CA, USA), a Rheodyne 9010 polyether ether ketone (PEEK) liquid six-port injection valve (Rheodyne, Cotati, CA, USA), fitted with a 100-μl PEEK sample loop. The analytical column was a PEEK (50×4.6 mm I.D.) casing, slurry packed with 5 μm particle size silica bonded with aminophosphonic acid using isopropanol under a constant pressure of 2000 p.s.i. on a Shandon packing ma-

chine (Shandon Southern Products, Cheshire, UK) (1 p.s.i.=6894.76 Pa).

The post-column detection system included a Constametric III HPLC pump (LDC, Riviera Beach, FL, USA) to deliver the post-column reagent (PCR), a zero dead volume PTFE tee and a 1.4 m×0.3 mm I.D. PTFE reaction coil. Detection was achieved using a spectral array detector (Dionex) set at 560 nm.

2.2. Reagents

The optimised PCR used in this study was a mixture of 0.008% Chrome Azurol-S (CAS), 1 *M* hexamine and 10 m*M* ethylenediaminetetraacetic acid (EDTA) buffered at pH 6. A 1 *M* KNO_3, 0.5 *M* HNO_3 and 0.08 *M* ascorbic acid solution was used as the eluent. Both the eluent and PCR were delivered at 1 ml min^{-1}.

All reagents were of AnalaR grade (BDH, Poole, UK), with the exception of CAS (65% dye content) (Aldrich, Gillingham, UK).

1000 mg l^{-1} metal stock solutions (BDH) were diluted to working standards using distilled deionised water (Milli-Q, Millipore, Milford, MA, USA), and stored in poly(propylene) bottles (BDH).

2.3. Sorbent

The aminophosphonic acid (APAS) was synthesised as described earlier [20], by reaction of aminopropylsilica with hypophosphorous acid and formaldehyde.

The structure of APAS is shown in Fig. 1.

2.4. Sample pretreatment

The sample was prepared using sodium hydroxide fusion. From a previous study [21], and our own investigations, HF digestion with borate addition is not suitable for the determination of Be(II) by IC, due to the formation of a stable beryllium fluoride complex which prevents a post-column reaction detection system from operating effectively.

For the fusion procedure, a known amount of accurately weighed sample (0.5 g) was added to a nickel crucible in which 5 g of NaOH had been fused and allowed to cool. The crucible was heated to fusion and a temperature of about 500°C maintained for 45 min, after which it was ice-cooled. The fusion melt was treated with ice cooled Milli-Q water and transferred to a volumetric flask. Sufficient nitric acid added was added to attain approximately 0.5 *M* after neutralisation of the alkali and final dilution to 50 ml.

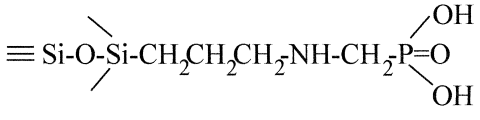

Fig. 1. The structure of aminomethylphosphonic acid group bonded to silica.

3. Results and discussion

3.1. Retention characteristics and selectivity of beryllium on APAS

The aminomethylphosphonic acid group has a number of chelating possibilities. At low pH the acidic POH groups would be the principal chelating ligands and at higher pH the basic amino nitrogen could become additionally involved, as discussed in Refs. [22,23]. However, APAS can also act as a cation exchanger in weak acid or neutral solutions through dissociation of its phosphonic acid groups [20]. Therefore, a high concentration of KNO_3 was used within the mobile phase to suppress any retention that may arise due to simple ion exchange and ensure that ''chelation exchange'' was the dominant retention mechanism.

A short study was undertaken to determine whether the ionic strength of the sample would have an effect upon the metal retention characteristics. This was investigated through the injection of a standard transition metal mixture of Ni(II), Zn(II), Cd(II) and Mn(II) prepared in solutions of widely varying ionic strength, at pH 2.3. The resultant overlaid chromatograms of the metal mixture in deionised water and 2 *M* KNO_3, as illustrated in Fig. 2, show that the retention times for each metal remain virtually unchanged in spite of a massive change in ionic strength. In addition, peak broadening does not appear to occur, with each metal peak remaining sharp and fully resolved. This result is a

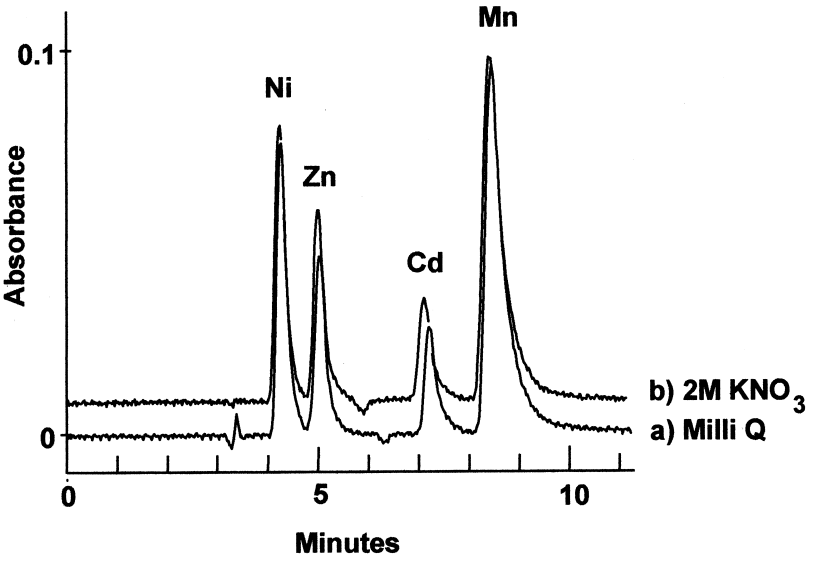

Fig. 2. The effect of sample ionic strength: (a) Milli-Q, (b) 2 *M* KNO_3 on the separation of a group of metals, Ni, 0.5 mg l^{-1}; Zn, 0.5 mg l^{-1}; Cd, 2 mg l^{-1} and Mn, 0.5 mg l^{-1}. Eluent, 1 *M* KNO_3, 5 m*M* HNO_3. Column, 250×4.6 mm, containing aminomethylphosphonic acid bonded to 5 μm silica.

good example illustrating the insensitivity of HPCIC to large changes in ionic strength and also indicates that any possible simple ion exchange interaction is strongly suppressed.

A detailed study of the retention of beryllium on APAS was carried out and the log k' versus pH plot, as shown in Fig. 3, follows the same trend for the other Group IIa alkaline earth metals investigated previously [19], in that an S-shaped dependence was observed. As Be has a greater affinity for oxygen than for nitrogen, with the stability of complexes containing N,O ligands being lower than those of O,O donors [24,25], this change in the curve is probably due to the onset of the second acid dissociation step of the methylphosphonic acid group on APAS, which occurs in the pH range 2–3. It is proposed that this dissociation results in a change in the co-ordination between the phosphonic acid group and the metal, from two oxygen atoms on the phosphonic acid group to all three. This was similarly postulated for the other alkaline earth metals [19].

When considering the stability constants for metal ions complexing with methylphosphonic acid in homogeneous solution, which should be analogous to the APAS bonded group at low pH, the log K_1 value for beryllium is relatively large compared to other +2 metal ions (cf. log K_1 values for Be and Cu which are 6.3 and 3.5, respectively [26,27]). This finding is reflected in the beryllium ion's behaviour on APAS giving a much stronger retention than all the +2 ions, including copper, which is normally the strongest retained. The +3 metals would be expected to show a stronger affinity for APAS compared to +2 ions including beryllium, but interestingly, as shown in Fig. 3, although the lanthanides show the expected increase in affinity, Al(III) is rather weakly retained. This could be due to the fact that the very small size of the Al(III) ion does not allow a ''good fit'' into the rather rigid structure of the P–O bonds of the phosphonate group. Fe(III), which is not shown, has a particularly strong interaction with the APAS substrate, reflecting the special affinity of ferric ions for P–O bonds.

A rather unexpected characteristic of beryllium retention on APAS is the peak shape. Virtually all studies involving HPCIC show peak shapes which are quite sharp close to the solvent front, but rapidly broaden with increase in retention time. This rapid broadening is as a result of slower kinetics of dissociation of the metal complexes on the chelating substrate as conditional stability constants increase. Furthermore, the increase in broadening is accom-

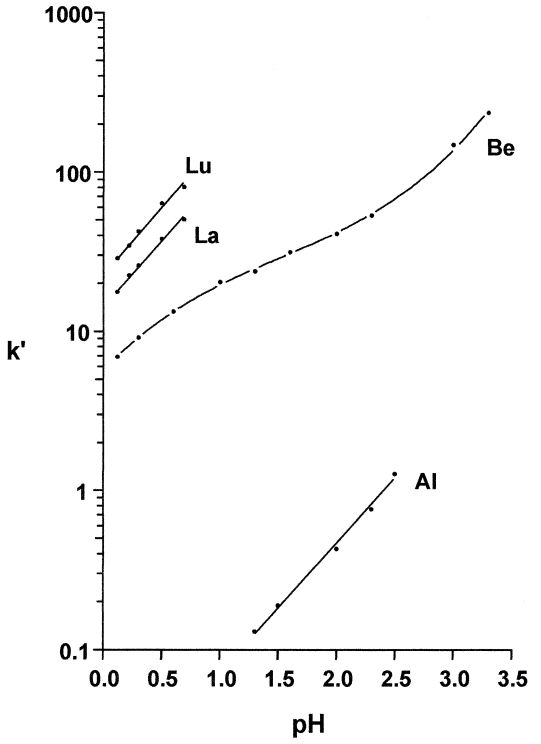

Fig. 3. k' versus pH plot of Be(II), La(III), Lu(III) and Al(III) on a column containing aminomethylphosphonic acid bonded to 5 μm silica. Eluent, 1 *M* KNO_3.

panied by an increase in peak asymmetry. However, for beryllium, the peak shape does not show this trend. Firstly, the peak is broader than normal at short retention times and does not broaden that much with increase in retention time and secondly, good peak symmetry is maintained regardless of the retention time. These characteristics are surprising and difficult to explain from the thermodynamic and kinetic properties of complex formation and dissociation.

3.2. Method development

3.2.1. Separation conditions

As discussed above the special selectivity of APAS for beryllium means that the peak should be well separated from other +2 metal ions. When considering sediment samples, there will also be present large amounts of Al(III) and Fe(III) after digestion. Fig. 3 shows that beryllium should be completely separated from Al(III) as it is essentially unretained at low pH. The main problem is the presence of Fe(III). It is very strongly retained even at high acidities and elutes slowly from the column giving rising baselines. To solve this problem ascorbic acid was added to the mobile phase so that any Fe(III) injected with the sample would be reduced to Fe(II) on-column and elute close to the dead volume. The presence of ascorbic acid in the eluent also prevented build-up of Fe(III) on the column due to trace impurities in the reagents.

An acid concentration in the mobile phase of 0.5 *M* was finally chosen, as this gives a retention time of about 5 min for beryllium, ensuring an efficient analysis time. In addition, from this and previous studies [19], the transition and heavy metals, aluminium and the alkaline earth metals are unretained on the APAS substrate at this pH. The lanthanides, although more strongly retained than Be should not be present in significant amounts and in any case do not react with the post-column reagent [25].

It is appropriate at this point to comment on the stability of the substrate. Silica becomes increasingly soluble at high pH and the stability of certain bonded groups can be affected at low pH. At the acid concentrations used here, there was little indication of silica dissolution even after extended use over 12 months. The aminophosphonate bond to silica was also found to stable at these low pH values with only a slight decrease in capacity over the period of the study.

3.2.2. Detection conditions

CAS was chosen as the post-column reagent as it is one of the most sensitive chromogenic ligands for the determination of Be(II), forming a 1:1 complex in the pH range 3.5–5.0 [28]. To establish the feasibility of using CAS in this system, a calibration of Be(II) over the concentration range 20 μg l^{-1} to 5 mg l^{-1} was carried out. The PCR conditions were, 0.008% CAS, 1 *M* hexamine buffered to pH 6, which when combined with an eluent composed of 1 *M* KNO_3 and 0.5 *M* HNO_3, resulted in an effluent pH of 5.3. The linearity of the system was good with a regression coefficient of $R^2=0.9986$ using peak area. The relative standard deviation (RSD) for the repeat injection ($n=6$) of a 1 mg l^{-1} working

standard was 1.24%, and the detection limit was calculated as 13 μg l^{-1} using two-times the average peak-to-peak noise.

In spite of the good selectivity of APAS for Be, the very high concentration of metals present in the sample, even after the 100-times dilution factor during pretreatment, meant the Be peak became partly obscured within the accumulated massive tailing of these unretained metals. To solve this problem and still allow the sensitive detection of Be, EDTA was added to the PCR as a masking agent. EDTA complexes rather weakly with Be, but much more strongly with those metals reacting with CAS. A short study showed that the Be signal was barely affected by EDTA, but the detector response of the other metals was severely reduced. A concentration of 10 m*M* EDTA in the PCR was found sufficient to reduce the peak and subsequent tailing of a suite of metals which would elute on the solvent front and interfere with the Be(II) peak. Loss of the Be(II) signal due to complexation with EDTA was negligible at this concentration. A calibration of Be(II) over the range 50 μg l^{-1} to 5 mg l^{-1}, in the presence of a suite of unretained metals in the proportions as found in the diluted reference material, namely Al(III), 500 mg l^{-1}; Fe(III), 300 mg l^{-1}; Mn(II), 25 mg l^{-1}; Zn(II), 4 mg l^{-1} and Cu(II), 1 mg l^{-1}, resulted in a regression coefficient of $R^2=0.9994$ using peak area. The RSD for the repeat injection ($n=6$) of a 1 mg l^{-1} Be(II) standard in the presence of the unretained metal suite (880 mg l^{-1}) was 4.81%. A detection limit of 35 μg l^{-1} was calculated, using the same method as before. A typical separation of 5 mg l^{-1} Be(II) from the unretained metal suite is shown in Fig. 4.

The effect of fluoride concentration in the sample on the Be signal was also investigated, as the complex ion $[BeF_4]^{2-}$ can exist in acid solution. The fluoride concentration in the reference material was certified at 1250±61 mg kg^{-1}. In the presence of 500 mg l^{-1} [F^-], the signal for a 1 ppm Be standard, under optimum eluent and PCR conditions, was reduced by more than 50%. At 50 mg l^{-1} [F^-] in the sample however, there was no noticeable reduction in the signal for Be. Taking into consideration the dilution factor during sample pretreatment, and the presence of other matrix elements which could possibly complex with the fluoride ion, it was decided that the presence of this halide in the sample as a source of analyte loss would be negligible. However, fluoride levels should be taken into consideration when applying this method to other sample types.

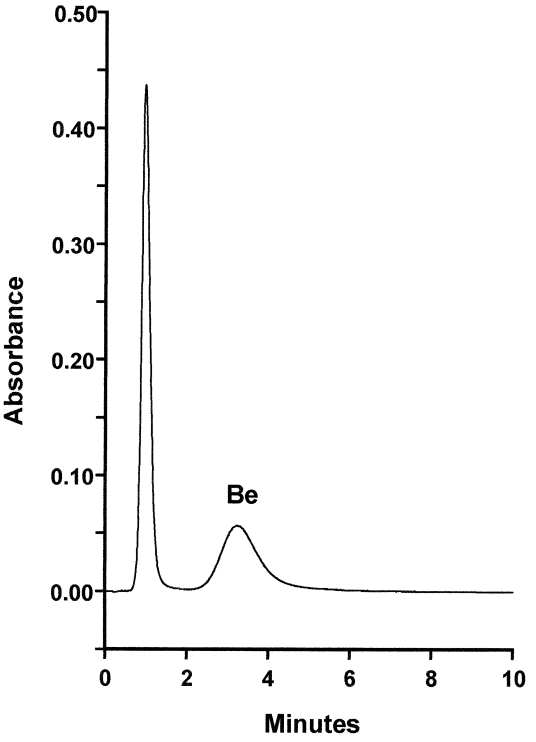

Fig. 4. The separation of Be(II), 5 mg l^{-1}, from Al(III), 500 mg l^{-1}; Fe(III), 300 mg l^{-1}; Mn(II), 25 mg l^{-1}; Zn(II), 4 mg l^{-1} and Cu(II), 1 mg l^{-1}. Column, 50×4.6 mm. Eluent, 1 *M* KNO_3, 0.5 *M* HNO_3 and 0.08 *M* ascorbic acid.

3.3. Analytical performance characteristics

The accuracy of the proposed method was tested by the determination of beryllium in a certified stream sediment, GBW07311 (26±4 mg kg^{-1} certified concentration). Replicate sample analysis with a standard addition calibration plot using peak area, $R^2=0.999$, gave a mean result ($n=4$) of 26.3±0.4 mg kg^{-1}, which compared well with the certified value. The reproducibility (RSD) of the method was ascertained with the repeat injection ($n=6$) of the sample, and was found to be 2.05% using peak area.

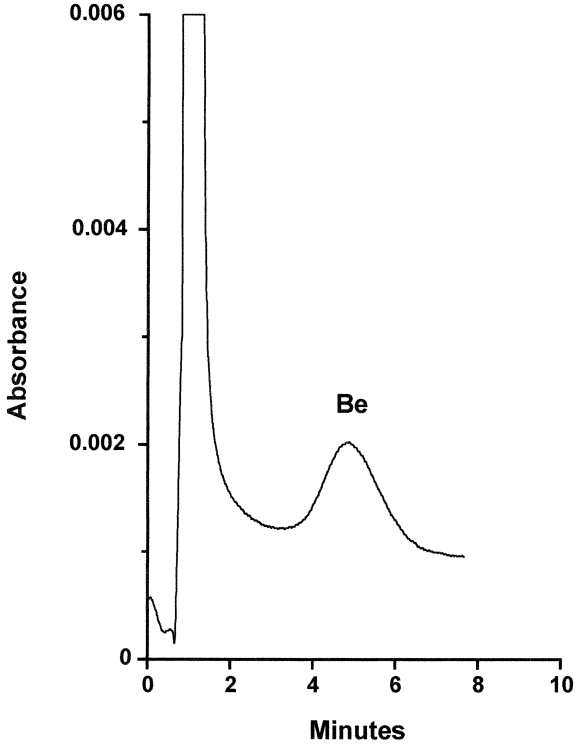

Fig. 5. The separation of beryllium from matrix metals in a certified reference material (GBW07311). Column as in Fig. 2. Eluent, 1 *M* KNO_3, 0.5 *M* HNO_3 and 0.08 *M* ascorbic acid.

A chromatogram of a sample injection is shown in Fig. 5.

4. Conclusions

A selective and sensitive HPCIC method for the determination of Be(II) in complex sample matrices has been developed. Using a small particle size silica, chemically modified with aminomethylphosphonic acid as a chelating substrate, trace levels of beryllium could be separated from the massive excess of matrix metals using isocratic elution. The results achieved for the stream sediment sample compared well with the certified value, which shows that this system is a useful alternative to atomic spectrometric techniques.

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